The Contribution of Black Carbon to Bulk Lake Superior Sediment

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1. Introduction

Black carbon (BC) is the heterogeneous, aromatic, and carbon rich residue of fossil fuel combustion and biomass burning. BC is classified as carcinogenic aromatic organic compounds. The burning of biomass and combustion of fossil fuels produce olithic aromatic structures called soot. Char is also a by-product in the reactions but poses a less ordered structure. Both by-products form simultaneously and commonly coexist in sediment and soil samples. The term graphitic carbon has been used to refer to black carbon, as the microcrystalline structure is similar to graphite. Black carbon is of interest to researchers for three main reasons: BC isotopic analysis correlates to the fire history of a given area; BC is a good absorbent of polycylic aromatic hydrocarbons (PAHs); and there are health hazards associated with BC.

Large BC particles concentrate in sediment and soils while, soot particles are aerosols and are transported to oceans ultimately becoming fine particulate organic matter or dissolved organic matter (DOM , operationally defined as <0.7 or <0.2 μm) and being deposited in marine sediment. According to (Hammes et al., 2007), greater than 80% of BC produced ends up in the soil where it can reside for hundreds to thousands of years as it is relatively resistant to chemical and biological decomposition. The developed methods for quantifying BC in the soil and sediment rely on its resistance to degradation. The burning of biomass produces various sized particles and the size correlates to the transportability; how far the particles can travel. A study done by Clark & Patterson (1997), found millimeter-size particles are no longer airborne within 100m of the source. Charlson and Ogren (1983) conducted an experiment, which showed aerosol particles have the ability to be airborne for months. Huang (2004) indicated BC larger than 2 mm in diameter do not become airborne, thus limiting long-distance transport capability. Large char particles do not become airborne and commonly are deposited in the sediment near the source. The fire history of a region can be achieved by BC measurements along with isotopic studies using lead 210 isotopes to look at sedimentation rates or short-term sediment ages and carbon 14 analysis of modern carbon in bulk sediment samples to look at longer term sedimentation rates and sediment ages. Knowing the concentration of BC in the dated sediment allows one to determine if significant fires occurred 100, 1000, or 10,000 years ago.

Another interesting characteristic of black carbon is its ability to interact with other chemicals. BC is capable of absorbing organic pollutants and heavy metals out of the atmosphere, water, and sediment. Albert Koelmans et al (2005) indicates BC is extremely efficient at absorbing highly toxic PAHs, polychlorinated biphenyls, dioxins, polybrominated diphenylethers, and pesticides out of soils and sediments. This characteristic may reduce the risk posed by organic contaminants in soils and sediments. Koelmans et al (2005) recognized BC catalyzes the

formation of nitrous acid in the atmosphere. The creation of nitrous acid contributes to the formation of photochemical ozone and smog.

A major issue associated with black carbon is its ability to absorb light energy and lower the reflectivity of albedo surfaces such as water, ice, and snow. This increases the melting of numerous glaciers at a much faster rate (Gustafsson et al., 2001). In addition, this property is a major contributor in global warming.

Scientists continue to conduct various studies on the biological effects of black carbon through clinical and animal testing. Humans and animals are mostly exposed to aerosol BC by inhalation in the immediate vicinity of local sources. Common indoor sources include candles and biomass burning, where the aerosol soot is produced from vehicles and is the major outdoor source. The World Health Organization (WHO) estimates that indoor smoke from solid fuels is among the top ten major risk factors globally, contributing to approximately 2 million deaths annually. When aerosol BC is inhaled the particles migrate into the lungs. As BC is a strong absorbent of toxic PAHs, the inhalence of BC leads to respiratory issues and has been linked to lung cancer.

In this study the chemothermal oxidation (CTO-375) method (Gustafsson et al., 2001) was used to analyze BC in Lake Superior sediment samples. The process is defined as three main steps, acidification to the ground dry sample to remove inorganic carbonates (IC), combusting samples in a muffle furnace at 375 C° to isolate the polyaromatic BC from the less condensed nonpyrogenic organic carbon (NPOC), and analyzing the samples with an elemental analyzer-infred mass spectroscopy (EA-IRMS).

2. Research Methodology

The contribution of BC to bulk Lake Superior sediment was achieved using the chemothermal oxidation method to isolate BC and an EA-IRMS instrument to subsequently analyze the organic concentration and the ratio of C12 and C13 isotopes (Gustafsson et al., 2001). The marine core sediment samples analyzed were taken at a water depth of 23.3 meters and at the following coordinates, 46° 43.85'N and 91° 59.11'W. The samples were freeze dried and ground to a homogeneous mixture in an agate mortar and pestle. An EA microbalance was used to record the capsule and sediment weights. Concentrated hydrochloric acid (HCl) was used to acid fumigate the samples to dissolve any inorganic carbonates deposited in the sediment. The samples were then combusted in a muffle furnace at 375 C° for 18hrs. Elemental and ^{13}C isotopic analysis was completed on an EA-IRMS instrument.

3. Findings

Averaged values of the samples' initial weight, black carbon weight, weight percent of carbon, and the standard deviation are presented in Table 1.

Sample ID and Depth	Initial Weight (mg)	BC weight in sample (mg)	Weight percent of BC (%)	Error (+-)
5NS 0-2	17.79	0.048	0.27	0.014
5NS 2-4	15.90	0.048	0.30	0.017

5NS 4-6	18.66	0.035	0.19	0.015
5NS Core 2 0-2	19.57	0.059	0.31	0.046
5NS Core 2 2-4	17.85	0.15	0.85	0.045

Table 1. Averaged values of 5NS and 5NS Core 2 samples at various depths

As shown in Figure 1 and Table 1, both sample sets (5NS and 5NS Core 2), show increased carbon amount at a depth of 2-4cm. Nist 1649b standards also known as urban dust were used to test our protocol. Table 2 presents the results from analyzing the combusted (C) and non-combusted (NC) standards.

Nist (C) 1649b Initial Weight (mg)	Nist (C) 1649b Black Carbon Weight (mg)	Nist (C) 1649b Weight Percent Black Carbon to Bulk Sample (Wt %)	Nist (NC) 1649b Initial Weight (mg)	Nist (NC) 1649b Carbon weight (mg)	Nist (NC) 1649b Weight Percent Total Organic Carbon to Bulk Sample (Wt %)
5.9	0.183	3.10	1.99	0.352	17.69 ± 0.026
4.58	0.106	2.31	1.85	0.331	17.89 ± 0.026
4.22	0.096	2.27	1.97	0.351	17.82 ± 0.026

Table 2. NIST 1649b standard carbon analysis results

Table 3 illustrates the results of previous work using urban dust and the CTO-375 method.

Author	Wt. % OC	Wt. %BC
Simpkins & Minor	17.77 ± 0.01	2.74 ± 0.01
Mannino & Harvey	17.96 ± 0.04	4.07 ± 0.14
Gustaffson et al.	17.60 ± 0.40	1.40 ± 0.14

Table 3. Previous NIST 1649a Urban Dust Analysis.

Our BC weight percent results on the urban dust standard match those of previous studies. Our lake sediment results are low compared to previous work using urban dust standards and the CTO-375 method. This may be due to the lack of anthropogenic activity within the Lake Superior watershed.

Using the obtained values (Table 1), a weight percent of black carbon to bulk sediment graph was generated and is presented as Figure 1.

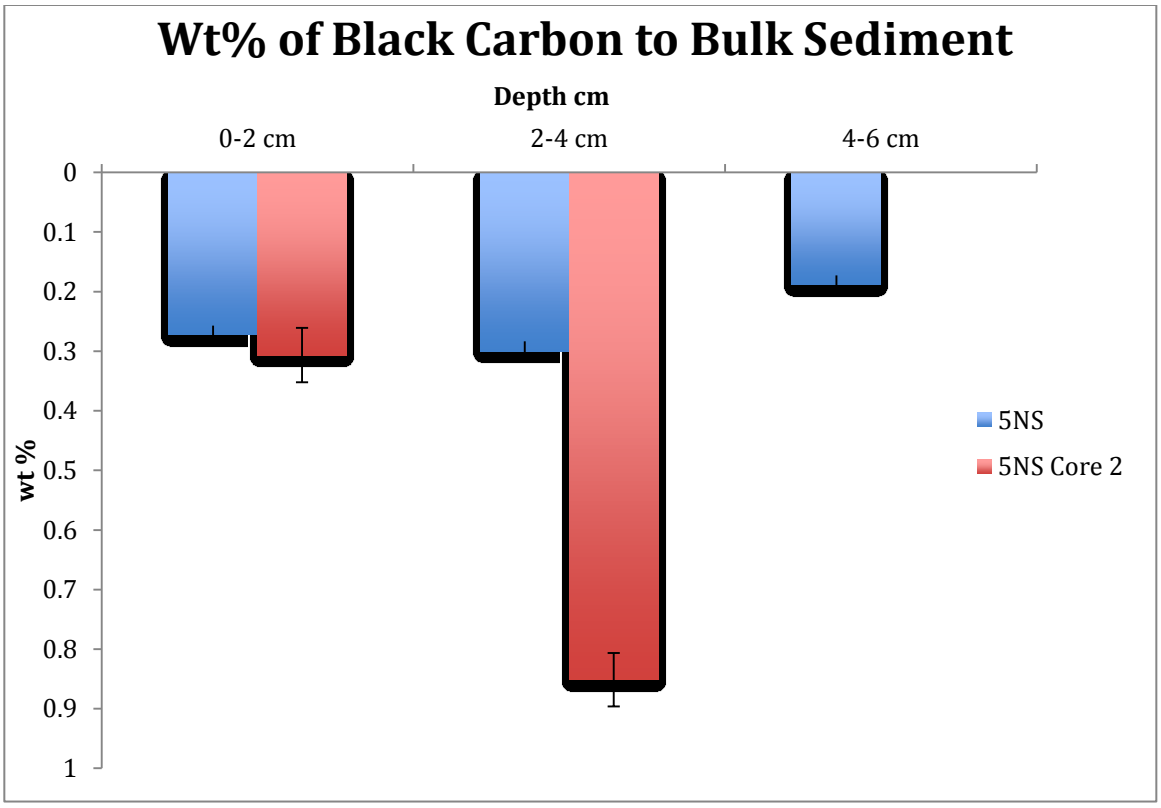

Figure 1. Weight percent of black carbon to the bulk sediment samples at various depths

All sediment samples had measurable BC. The increase in weight percent of black carbon at the depth of 2-4cm could indicate inputs from a fire.

4. Conclusion

The lake sediment samples taken at a water depth of 23.3 meters and at the following coordinates, 46° 43.85'N and 91° 59.11'W were analyzed by EA-IRMS. The following samples 5NS 0-2, 5NS 2-4, 5NS 4-6, 5NS core 2 0-2, and 5NS core 2 2-4cm had the following weight percent of black carbon, 0.27, 0.30, 0.19, 0.31, and 0.85%, respectively. The analyzed NIST urban dust standards showed weight percent of total organic carbon to bulk sediment samples of 17.69, 17.89, 17.82± 0.02, respectively while, the weight percent of BC to the NIST standards were, 3.10, 2.31, and 2.27± 0.02. The findings to the analysis were very similar to other published findings from Simpkins & Minor, Mannino & Harvey, and Gustaffson et al. Sources of error during this experiment include but are not limited to: in accurate EA-microbalance measurements, leaking capsules, and aerosol contamination during sample processing.

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